Translation of

11) Japanese Kokai Patent laid-open-to-public inspection No.: 60/226599 (1985)

43) Date of publication of unexamined document: November 11, 1985

21) Application No.: 59/83488 (1984)

22) Date of Application: April 25, 1984

51) International Classification[4]: C 11 D 3/386
//C 12 N 9/14
9/58
(C 12 N 9/14
C 12 R 1:845)
(C 12 N 9/58
C 12 R 1:845)

54) Title: DETERGENT COMPOSITION

71) Applicant: Kao Soap Co. Ltd.
10, 14, Kayabacho-1, Nipponbashi, Chuoku, Tokyo

72) Inventor(s): E. Hoshino
6-2606 Oaza Akabane, Ichigaicho, Hagagun, Tochigi

A. Nakaei
7-2-3, Miyashirodai, Miyashirocho, Saitamagun, Saitana

M. Murata
12-4-2, Izumigaoka, Utsunomiya City

Title: DETERGENT COMPOSITION

Claims:

1. A detergent composition containing cellulase produced by molds belonging to Rhizopus sp. and hydrolases excluding cellulase produced by molds belonging to Rhizopus sp.

2. A detergent composition as set forth in Claim 1, wherein the hydrolases excluding cellulase produced by molds belonging to Rhizopus sp. are one or more than one kind selected from the group consisting of hemicellulase, pectinase, amylase, and protease.

Remarks:

The combination of two or more enzymes exhibits remarkable detergency for the inorganic soil for which they are not effective when used individually.

SPECIFICATIONS

1. Title of the invention

Detergent composition

2. Patent Claims

1. Detergent composition containing cellulase produced by molds (Rhizopus sp.) and hydrolases, excluding cellulase, produced by molds (Rhizopus sp.).

2. Detergent composition according to Claim 1, characterized by the fact that the hydrolases, excluding cellulase, produced by molds belonging to Rhizopus sp. are 1 or more kinds selected from a group consisting of hemicellulase, pectinase, amylase and protease.

3. Detailed explanation of the invention

Industrial application

This invention is concerned with a detergent composition; more in detail, this invention is concerned with a detergent composition with excellent cleaning power by mixing 2 or more enzymes produced by Rhizopus sp. in the composition.

Previous techniques

Recently, the techniques of washing clothes have been developed significantly. Washing of clothes became easier by the development of suitable detergents, improvement of water quality, improvement of washing machines, fibers, etc. Particularly, the improvements that have been made in the detergent field was remarkable. It seems that the detergents for clothes are almost perfect due to improvements in surfactants, builders, dispersing agents, fluorescent dyes, bleaches, etc. The background ideas of detergents for clothes are are as follows:

1) adsorption of the surfactant or builder on the dirt and/or surface fibers decreases the surface tension between the dirt and/or fiber and water, then the dirt is removed from the fiber physically or chemically;

2) dispersion and solubilization of the dirt by the surfactant or inorganic builder;

3) chemical decomposition of the dirt by the use of enzymes, such as protease;

4) bleaching of colored dirt chemically;

5) increase of whiteness by the adsorption of fluorescent dyes on the surface of the fibers;

6) prevention of precipitation of divalent metal ions by chelating agents.

Problems solved by this invention

Previously, the basic idea of washing of clothes was the combination of a component to attack dirt and one to assist this attack as a component of the detergent. Currently, detergent compositions based on the abovementioned idea have reached their maximum capability and further increase would require immeasurable effort.

Methods to solve the problems posed

The inventors investigated the washing of clothes from a completely new point of view without considering previous concepts of washing and arrived at this invention by discovering unexpected washing effects obtained using a detergent composition containing cellulase produced by molds belonging to Rhizopus sp. and hydrolases excluding the cellulase produced by molds belonging to Rhizopus sp., selecting preferably 1 or more from hemicellulose, pectinase, amylase and protease. An extremely effective washing effect was found which was not related to the enzymatic activity of cellulase, hemicellulase, pectinase, amylase or protease.

This invention offers a detergent composition containing cellulase produced by Rhizopus sp. and hydrolases, excluding cellulase, produced by Rhizopus sp., which detergent composition produces a remarkable washing effect toward inorganic dirt, without relationship to these specific enzymatic activities.

It has been known that enzymes can be used in detergents. These enzymes used are effective only on organic dirt. For example, protease has been used for protein-type dirt, amylase for starch and lipase for oils and fats. These enzymes work directly on the dirt.

Effect of the invention

The cleaning mechanism by the mixture containing 2 or more enzymes of cellulase and hydrolase, excluding cellulase, produced by Rhizopus sp., is not understood, but it is not based on a simple swelling action of the fiber by the detergent.

The advantage of this invention is in its washing effect on inorganic dirt, for example, fine mud, which is not washed out effectively by conventional detergents. This invented detergent is also effective on dirt on collars, sleeves, oil stains, etc., and this will improve the washing power of detergents containing phosphate builders (phosphate-containing detergents) or of low-phosphate detergents. Fine mud present between fibers is removed by phosphates. However, the environmental problems that phosphates cause forced us to decrease the phosphate content of detergents or even to use nonphosphate detergents. Thus, removal of mud became difficult. It is well known that mud stains on cotton are hard to remove. Mud on canvas made of mixed cotton fibers is a headache for housewives. The detergent of this invention attempts to solve these problems. When mud is attached to cellulose fibers and on cellulose fibers mixed with other fibers is washed, the detergent of this invention provides a better washing power or one equivalent to that of a weakly alkaline powder detergent that contains phosphate when using this invention with

1) alkaline detergent without phosphate or with a low phosphate content, or

2) weakly alkaline or neutral liquid detergents without phosphate.

The other advantage of this invention is that the cleaning capacity of this composition toward inorganic dirt is independent of pH. As it is well-known, enzymatic activity is maximum at the optimum pH. Cellulase, which has its optimum pH in the acidic region, still shows a sufficient cleaning power in the alkaline region. The strength of the fibers is not affected as compared to conventional detergents.

The biggest advantage of this invention is that it can be applied to any type of detergent. The abovementioned 2 or more specific enzymes produced by Rhizopus sp. can be added to any powder, tablet, liquid or other type of detergent.

Action

The specific action produced by Rhizopus sp., which enzymes are the essential components of this invention, are obtained from the following Rhizopus sp. (1)-(19) used as a mixture or purified material.

(1) Rhizopus nigricans
(2) R. fumaricans
(3) R. oryzae
(4) Chlamydomucor oryzae
(5) R. japonicus β amylomyces
(6) R. tonkinsis or γ-amylomyces
(7) R. formosensis
(8) R. javanicus
(9) R. Delemar
(10) R. Cambodia
(11) R. Tritici
(12) R. chinensis
(13) R. Batatas
(14) R. Oligosporus
(15) R. PêkaI
(16) R. PêkaII
(17) R. Tamiri
(18) R. chungkuoensis
(19) R. niveus
(20) R. salebrosus

In this invention, commercial enzymes from the following sources can be used:

(1) Macerozyme S, Yakult Chemical Company
(2) Uniase 30, Yakult Chemical Company
(3) Koclase·G_2, Sankyo Co. Ltd.
(4) Glucozyme, Nagase Sangyo Co. Ltd.
(5) Gluczyme, Amanoseiyaku Co. Ltd.
(6) Newlase, Amanoseiyaku Co. Ltd.
(7) Samprose, Hankyo Kyoei Bussan Company
(8) Glutase, Hankyo Kyoei Bussan Company
(9) Lipase·Saiken, Osaka Saikin Institute
(10) Sumizyme, Shin Nippon Kagaku

Among these commercial enzymes, (1) contains mainly pectinase and hemicellulase; (2), (3), (4), (5), (8) and (10) contain amylase; (6) and (7) contain protease; (9) contains lipase, but all of them include cellulase.

The detergent composition of this invention is prepared by mixing these enzymes with known detergent compositions. The amount of enzyme is 0.001 unit of cellulase and hydrolase, excluding cellulase, or more/mg of solid material (1 unit/mg of solid material is one which produces 1.0 μmole of product per hour at 37°C and pH 5), mixing 0.01-70 weight % into a detergent, more preferably, 0.1-10 weight %. The enzyme content is preferably 0.1-1000 units/L, more preferably, 1-100 units/L.

The detergent composition of this invention has no restrictions except that it contains specific enzymes produced by Rhizopus sp. and known detergent components in a mixture. For example, the following components can be added based on their own effects.

The following are examples of surfactants:

1) Straight or branched chain alkylbenzenesulfonates with alkyl groups having an average number of carbon atoms of 10-16.

2) Alkyl or alkenyl ether sulfate salts with straight or branched alkyl or alkenyl groups having an average of 10-20 carbon atoms and an average of 0.5-8 moles of ethylene oxide, propylene oxide, butylene oxide or a mixture of ethylene oxide and propylene oxide at a ratio of 0.1/9.9 - 9.9/0.1 or a mixture of ethylene oxide and butylene oxide at the ratio of 0.1/9.9 - 9.9/0.1 per molecule.

3) Alkyl or alkenyl sulfate salts with the alkyl or alkenyl groups having an average of 10-20 carbon atoms.

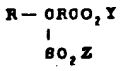
4) Olefin sulfonates with an average of 10-20 carbon atoms per molecule.

5) Alkanesulfonates with an average of 10-20 carbon atoms per molecule.

6) Saturated or unsaturated fatty acid salts with an average of 10-24 carbon atoms per molecule.

7) Alkyl or alkenyl ether carbonates with the alkyl or alkenyl groups having an average of 10-20 carbon atoms and with an average of 0.5-8 moles of ethylene oxide, propylene oxide, butylene oxide, a mixture of ethylene oxide and propylene oxide at the ratio of 0.1/9.9 - 9.9/0.1 or a mixture of ethylene oxide and butylene oxide at the ratio of 0.1/9.9 - 9.9/0.1 per molecule.

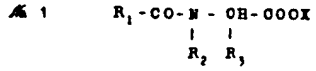
8) α-Sulfo fatty acid salts or esters as given by the following formula



(where Y is an alkyl group having 1-3 carbon atoms, or a counter ion and Z is a counter ion. R represents an alkyl or alkenyl group having 10-20 carbon atoms.)

The counter ions to the anionic surfactant can be alkali metal ions, such as sodium and potassium, alkaline earth metal ions, such as calcium and magnesium, ammonium ions and alkanolamines containing 1-3 alkanol groups having 2-3 carbon atoms) (for example, monoethanolamine, diethanolamine, triethanolamine and triisopropanolamine).

9) Amino acid-type surfactants described by the general formula as follows:



(where R_1 stands for alkyl or alkenyl groups with 8-24 carbon atoms, R_2 is a hydrogen or alkyl group having 1-2 carbon atoms, R_3 is an amino acid residue and X represents an alkali metal or an alkaline earth metal ion).

化 2 $R_1-CO-N-(CH_2)_n-COOX$ (with R_2 on N)

(where R_1, R_2 and X have the same meaning as given above and n represents an integer from 1-3).

化 3 $R_1R_1>N-(CH_2)_m-COOX$

(where R_1 is the same as described above and m represents an integer of 1-8).

化 4 $R_1-N(R_4)-CH(R_2)-COOX$

(where R_1, R_2 and X are the same as described above, R_4 represents a hydrogen or an alkyl or hydroxyalkyl group with 1-2 carbon atoms).

化 5 $R_1-N(R_2)-CH(R_3)-COOX$

(where R_2, R_3 and X are the same as described above, R_1 represents a β-hydroxyalkyl or β-hydroxyalkenyl group with 6-28 carbon atoms).

化 6 $R_5R_5>N-CH(R_3)-COOX$

(where R_3, R_5 and X are the same as described above).

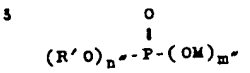
10) Phosphate ester type series active agents:

化 1 $(R'O)_{n'}-P(=O)-(OH)_{m'}$

alkyl or alkenyl acid phosphate esters
(where R' is an alkyl or alkenyl group with a carbon number 8-24, $n' + m' = 3$, $n' = 1-2$).

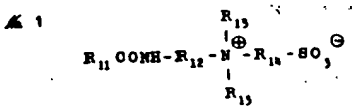
化 2 $(R'O)_{n'}-P(=O)-(OH)_{m'}$

Alkyl (or alkenyl) phosphoric acid esters
(where R' is the same as described above, n'' + m'' = 3, n'' = 1-3).

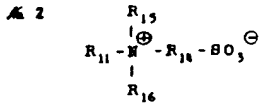


Alkyl (or alkenyl) phosphate ester salts
(where R', n'' and m'' are the same as described above, and M is Na, K or Ca).

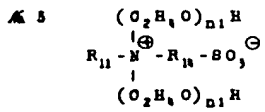
11) Sulfonic-acid-type amphoteric surfactants corresponding to the general formula given below:



(where R_{11} is an alkyl or alkenyl group consisting of 8-24 carbon atoms, R_{12} is an alkylene group consisting of *carbon atoms, R_{13} is an alkyl group having 1-5 carbon atoms and R_{14} is an alkylene or hydroxyalkylene group having 1-4 carbon atoms). (* 1-4)

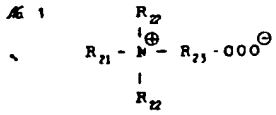


(where R_{11} and R_{14} are the same as described above, R_{15} and R_{16} are alkyl or alkenyl groups with 8-24 or 1-5 carbon atoms, respectively.

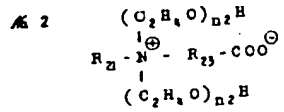


(where R_{11} and R_{14} are the same as described above and n_1 represents an integer of 1-20).

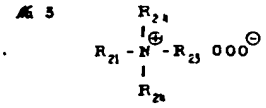
12) Betaine-type amphoteric active agents:



(where R_{21} is an alkyl, alkenyl, β-hydroxyalkyl or β-hydroxyalkenyl group having 8-24 carbon atoms, R_{22} is an alkyl group having 1-4 carbon atoms and R_{23} stands for an alkylene or hydroxyalkylene group with 1-6 carbon atoms).



(where R_{21} and R_{23} are the same as described above and n_2 represents an integer of 1-20).



(where R_{21} and R_{23} are the same as described above and R_{24} is a carboxyalkyl or hydroxyalkyl group having 2-5 carbon atoms).

13) Polyethylene alkyl or alkenyl ethers with alkyl or alkenyl groups having an average of 10-20 carbon atoms with 1-20 moles of ethylene oxide added.

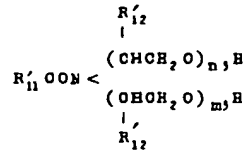
14) Polyoxyethylene alkylphenyl ethers with alkyl groups having an average of 6-12 carbon atoms and with 1-20 moles of ethylene oxide added.

15) Polyoxypropylene alkyl or alkenyl ethers with alkyl or alkenyl groups having an average of 10-20 carbon atoms and with 1-20 moles of propylene oxide added.

16) Polyoxybutylene alkyl or alkenyl ethers with alkyl or alkenyl groups consisting of an average of 10-20 carbon atoms and with 1-20 moles of butylene oxide added.

17) Nonionic active agents with alkyl or alkenyl groups having an average of 10-20 carbon atoms and with a total of 1-30 moles of ethylene oxide and propylene oxide or ethylene oxide and butylene oxide added (the ratio of ethylene oxide to propylene oxide or butylene oxide is 0.1/9.9 - 9.9/0.1).

18) Higher fatty acid alkanolamides or their alkylene-oxide addition compounds

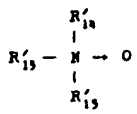


(where R'_{11} is an alkyl or alkenyl group having 10-20 carbon atoms, R'_{12} is H or CH_3, n_3 is an integer of 1-3 and m_3 is an integer of 0-3).

19) Sucrose fatty acids containing sucrose and fatty acids having an average number of 10-20 carbon atoms.

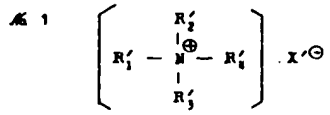
20) Fatty acid glycerol monoesters containing glycerol and fatty acids having an average number of 10-20 carbon atoms.

21) Alkylamine oxides represented by the general formula below

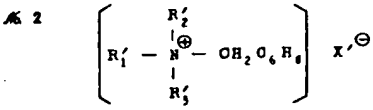


(where R'_{13} represents alkyl or alkenyl groups having 10-20 carbon atoms, R'_{14} and R'_{15} are alkyl groups having 1-3 carbon atoms).

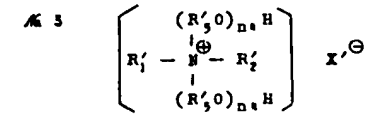
22) Cationic surfactants represented by the general formula given below



(where at least one of R'_1, R'_2, R'_3, R'_4 is an alkyl or alkenyl group having 8-24 carbon atoms, while the others are alkyl groups having 1-5 carbon atoms. X' represents a halogen).



(where R'_1, R'_2 and R'_3 and X' are the same as described below).



(where R'_1, R'_2 and X' are the same as described before and R'_3 is an alkylene group having 2-3 carbon atoms and n_4 represents an integer of 1-20).

In order to obtain a good effect, it is preferable for the composition to contain 10 weight % or more of at least 1 surfactant.

We can cite 1), 2), 3), 4), 5), 6), 11), No. 2, 12), No. 1,13) 14), 15), 17) and 18) as preferable surfactants.

In addition, the following component(s) can be added, depending on the purpose and necessity.

[1] Agents that trap divalent metal ions

Builder components (0-50 weight %) consisting of 1 or 2 or more of alkali metal salts, alkanolamine salts, as mentioned below, can be added.

1) Phosphoric acid salts, such as orthophosphate, pyrophosphates, tripolyphosphates, metaphosphates, hexametaphosphates and phytates.

2) Phosphonic acids and their derivatives, such as ethane-1,1-diphosphonic acid, ethene-1,1,2-triphosphonic acid and ethane-1-hydroxy-1,1-diphosphonic acid; phosphonic acid salts of the following acids, such as ethenehydroxy-1,1,2-triphosphonic acid, ethene-1,2-dicarboxy-1,2-diphosphonic acid and methanehydroxyphosphonic acid.

3) Phosphonocarboxylic acid salts of the following acids: 2-phosphonobutene-1,2-dicarboxylic acid, 1-phosphonobutane-2,3-4-tricarboxylic acid and α-methylphosphonosuccinic acid.

4) Amino acid salts, such as derived from aspartic acid and glutamic acid, glycine.

5) Aminopolyacetic acid salts, such as nitrilotriacetates, ethylenediaminetetraacetates, diethylenetriaminetetraacetates, iminodiacetates, glycol ether diaminetetraacetates, hydroxyethyliminodiacetates and diene cholates.

6) High-molecular electrolytes, such as polyacrylic acid, polyaconic acid, polyitaconic acid, polycitraconic acid, polyfumaric acid, polymaleic acid, polymethaconic acid, poly-α-hydroxyacrylic acid, polyvinyl phosphonic acid, sulfonated polymaleic acid, copolymer of maleic anhydride and diisobutylene, copolymer of maleic anhydride and styrene, copolymer of maleic anhydride and methylvinyl ether, copolymer of maleic anhydride and ethylene, copolymer of maleic anhydride and ethylene (crosslinked) copolymer of maleic anhydride and vinyl acetate, copolymer of maleic anhydride and acrylonitrile, copolymer of maleic anhydride and acrylic acid ester, copolymer of maleic anhydride and butadiene, copolymer of maleic anhydride and isoprene, poly-β-ketocarbonic acid derived from maleic anhydride and carbon monoxide, copolymer of itaconic acid and ethylene, copolymer of itaconic acid and aconitic acid, copolymer of itaconic acid and maleic acid, copolymer of itaconic acid and acrylic acid, copolymer of malonic acid and methylene, copolymer of metaconic acid and fumaric acid, copolymer of ethylene glycol and ethylene terephthalate, copolymer of vinylpyrrolidone and vinyl acetate, copolymer of 1-butene-2,3,4-tricarboxylic acid, itaconic acid and acrylic acid, polyester polyaldehyde carboxylic acid containing tertiary ammonium groups, cis-isomer of epoxysuccinic acid, poly[N,N-bis(carboxymethyl)acrylamide], poly(oxycarboxylic acid), starch succinic acid, starch maleic acid, starch terephthalic acid, ester, starch phosphoric acid ester, dicarboxy starch, dicarboxymethyl starch and cellulosesuccinic acid ester.

7) Nondissociating high-molecular compounds, such as polyethylene glycol, polyvinyl alcohol, polyvinyl pyrrolidone and cold-water-soluble urethanated polyvinyl alcohol.

8) Salts of dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, decane-1,10-dicarboxylic acid; salts of acids, such as diglycolic acid, thiodiglycolic acid, oxaloacetic acid, oxydisuccinic acid, carboxymethyloxysuccinic acid and carboxymethyltartronic acid; salts of hydroxycarboxylic acids, such as glycolic acid, malic acid, hydroxypivalic acid, tartaric acid, citric acid, lactic acid, gluconic acid, mucic acid, glucuronic acid and dialdehyde starch oxide; salts of itaconic acid, methylsuccinic acid, 3-methylglutaric acid, 2,2-dimethylmalonic acid, maleic acid, fumaric acid, glutamic acid, 1,2,3-propanetricarboxylic acid, aconitic acid, 3-butene-1,2,3-tricarboxylic acid, butane-1,2,3,4-tetracarboxylic acid, ethanetetracarboxylic acid, ethenetetracarboxylic acid, n-alkenylaconitic acid, 1,2,3,4-cyclopentanetetracarboxylic acid, phthalic acid, trimesic acid, hemimellitic acid, pyromellitic acid, benzenehexacarboxylic acid, tetrahydrofuran-1,2,3,4-tetracarboxylic acid and tetrahydrofuran-2,2,5,5-tetracarboxylic acid; salts of sulfonated carboxylic acids derived from acids, such as sulfoitaconic acid, sulfotricarballylic acid, cysteic acid, sulfoacetic acid and sulfosuccinic acid; carboxymethylates from sucrose, lactose and raffinose, carboxymethylated pentaerythritol, carboxymethylate of gluconic acid, condensates of polyalcohols or sugars with maleic anhydride or succinic anhydride, condensates of oxycarboxylic acids with maleic anhydride or succinic anhydride, organic acid salts such as CMOS and builder M, etc.

9) Aluminosilicates

No. 1. Crystalline aluminosilicates shown by the following formula

$$x'(M'_2O\text{又は}M''O)\cdot Al_2O_3\cdot y'(SiO_2)\cdot w'(H_2O)$$

(where M' is an alkali metal atom, M'' is an alkaline earth metal atom, exchangeable with calcium, x', y' and w' represent the number of moles of each component; generally $0.7 \leq x' \leq 1.5$, $0.8 \leq y' \leq 6$, and w' is an arbitrary positive number).

No. 2. Compounds represented by the following general formula are especially preferable as washing agent builders.

$$Na_2O\cdot Al_2O_3\cdot nSiO_2\cdot wH_2O$$

(where both n and w are numbers, n 1.8-3.0 and w 1-6).

No. 3. Amorphous aluminosilicates, represented by the following formula

$$x(M_2O)\cdot Al_2O_3\cdot y(SiO_2)\cdot w(H_2O)$$

(where M is a sodium and/or potassium atom, x, y and w represent the number of moles of each component within the following ranges:

$$0.7 \leq x \leq 1.2$$

$$1.6 \leq y \leq 2.8$$

and w is an arbitrary positive number of 0).

No. 4. Amorphous aluminosilicates represented by the following formula

$$X(M_2O)\cdot Al_2O_3\cdot Y(SiO_2)\cdot Z(P_2O_5)\cdot\omega(H_2O)$$

(where M is Na or K, X, Y and ω represent the number of moles of each component in the following ranges:

$$0.20 \leq X \leq 1.10,\quad 0.20 \leq Y \leq 4.00,$$
$$0.001 \leq Z \leq 0.80,$$

and ω is an arbitrary positive number of 0).

[2] Alkaline reagents or inorganic electrolytes

Further, as alkaline reagents or inorganic electrolytes, 1, 2 or more of each of the alkali metal salts mentioned below can be added to the composition in an amount of 1-50 weight %, preferably at 5-30 weight %. They are silicates, carbonates and sulfates; as organic alkaline reagents, one can cite triethanolamine, diethanolamine, monoethanolamine and triisopropanolamine.

[3] Agents protecting against recontamination

Further, agents that protect against recontamination can be added, namely, 1, 2 or more of the compounds shown below may be contained in the composition of 0.1-5%. These are polyethylene glycol, polyvinyl alcohol, polyvinyl pyrrolidone and carboxymethylcellulose.

Particularly, carboxymethylcellulose and/or polyethylene glycol with 2 or more enzymes produced by Rhizopus sp. of this invention show effective removal of muddy dirt.

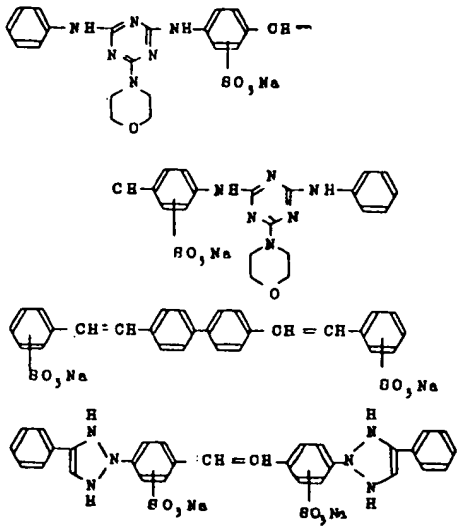
To prevent decomposition of carboxymethylcellulose by the cellulase during washing, it is desirable to granulate or coat the carboxymethylcellulose.

[4] Bleaches

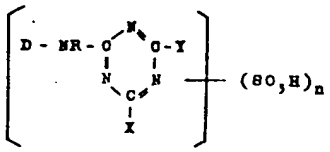
The washing effect is further enhanced when the present invented cellulase is used jointly with bleaching reagents, such as sodium percarbonate, sodium perborate, the addition compound between sodium sulfate and hydrogen peroxide and the addition compound between sodium chloride and hydrogen peroxide and/or photosensitive bleaching dyes, such as sulfonated zinc phthalocyanine or its aluminum salts.

[5] Blue tinting agents and fluorescent dyes

Many kinds of blue tinting agents and fluorescent dyes can be added, as necessary. For example, compounds with the following structures are recommended:

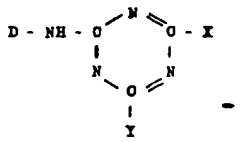


Blue tinting agents are shown by the formula given below.



(in the formula, D represents a monoazo, bisazo or anthraquinone series dye residue with blue or violet color; X and Y are hydroxyl groups, amine groups, hydroxyl groups*), sulfonic acid groups, carboxylic acid groups; the following with or without substitution by alkyl groups: aliphatic amino groups, halogen atoms, hydroxyl groups, sulfonic acid groups, carboxylic acid groups and lower alkyl groups; aromatic or cycloaliphatic amino groups with or without substitution by lower alkoxy groups. R is a hydrogen atom or a lower alkyl group, except when R is a hydrogen atom and (1) X and Y are hydroxyl groups or alkanolamine groups at the same time, (2) one of X or Y is a hydroxyl group and the other is alkanolamine; n is an integ r larger than 2).

*) Repeated in the Japanese text. - Translator.



(in the formula, D represents azo or anthraquinone series dye residues with blue or violet color, X and Y are identical or different alkanolamine residues or hydroxyl groups).

[6] Anticaking agents

In the case of powdery washing agents, the following anticaking agents can be added: paratoluenesulfonic acid salts, xylenesulfonic acid salts, acetic acid salts, sulfosuccinic acid salts, talc, finely-powdered silica, clay, calcium silicate (for example, Microcel, made by Johns-Manville Co. Ltd.), calcium carbonate and magnesium oxide.

[7] Antioxidants

Antioxidants, such as tertiarybutylhydroxytoluene, 4,4'-butylidenebis-(6-tertiarybutyl-3-methylphenol), 2,2'-butylidenebis-(6-tertiarybutyl-4-methylphenol), monostyrene cresol, distyrene cresol, monostyrene phenol, distyrene phenol and 1,1'-bis-(4-hydroxyphenyl)cyclohexane.

[8] Blocking agents against inhibitors of enzymes produced by Rhizopus sp.

There are occasions when many enzymatic activities are inhibited by the presence of ions and compounds of copper, zinc, chromium, mercury, lead, manganese and silver. Many metal chelating agents and precipitating agents are effective against these inhibitors. The divalent trapping agents mentioned in Section [1] as arbitrary compounds and/or magnesium silicate and magnesium sulfate are good examples. Many enzymatic substrates and their analogs, antimetabolites, enzymatic reaction products and their analogs, trapping agents for atoms that act on active enzymatic sites, substances that are active toward the metal portion of coenzyme and cofactor, coenzyme analogs that react competitively with the coenzyme and enzyme proteins. Such compounds must be avoided as much as possible or direct contact of these compounds with the enzymes must be avoided, for example, by coating these compounds.

Strong chelating agents, such as ethylenediaminetetraacetates, anionic surfactants and cationic surfactants can act as inhibitors. These compounds can be present together with the enzymes if they are tabletted or coated.

Coating agents or coating methods can be applied as required.

[9] Solubilizing agents

Lower alcohols, such as ethanol, benzenesulfonates, lower alkylbenzenesulfonates, such as p-toluenesulfonate, glycols, such as propylene glycol, acetylbenzenesulfonates, acetamides, pyridine dicarboxylic acid amides, benzoates and urea are examples of solubilizing agents. The present invented detergent composition has no limitation on the pH range and can be used at a wide range from the acid to the alkaline side.

Practical Examples

The present invention is explained more specifically using practical examples as follows: In the examples, % means % by weight unless otherwise specified.

Practical Example 1

This example shows the effectiveness of a mixture of cellulase produced by Rhizopus sp. and 1 or 2 or more enzymes of hemicellulase, pectinase, amylase and protease produced by Rhizopus sp. against muddy soil.

1) detergent composition	(powder detergent) Mixture A	(liquid detergent) Mixture B
straight-chain sodium dodecylbenzenesulfonate	10%	---
sodium-α-olefin sulfonate (C_{16}-C_{18})	5	---
sodium alkyl ethoxy sulfate (C_{14}-C_{15}, $\overline{EO}$ = 15 moles)	2	25%
sodium alkylsulfate (C_{14}-C_{15})	3	---
soap (fatty acid sodium salt)	2	---
secondary alcohol ($\overline{C}_{13.5}$) ethoxylate ($\overline{EO}$ = 7)	---	25
sodium tripolyphosphate	10	---
crystalline sodium aluminosilicate (type 4A)	10	---
sodium silicate (JIS No. 2)	10	---
sodium carbonate	10	---
carboxymethylcellulose	1	1
polyethylene glycol (MW 6000)	1	1
fluorescent dye	0.4	0.3
sodium p-toluenesulfate	2	---
mirabilite (sodium sulfate•H_2O	balance	---
ethanol	---	8
blue coloring dye	---	0.05
water	10	balance
enzyme	3	2
fragrance	0.2	0.1

2) Clothes with muddy dirt (clothes soiled with artificial dirt)

Kanuma Horticulture red soil was dried at 120°C ± 5°C for 4 hours, pulverized, sieved through a 150 mesh sieve (100 μm) and dried at 120°C ± 5°C for 2 hours. About 150 g was dispersed in 1000 mL of "Barklane" and cotton No. 2023 was treated with this solution, then brushed to remove the excess solution and dirt (Patent Showa 55(1980)/26473).

A test piece, 10 cm x 10 cm, was prepared.

3) Washing method, washing conditions and evaluation

The detergent was dissolved in water with a hardness of 4° DH and 1 L of a 0.133% detergent solution was prepared. The cotton cloths, 5 pieces, soiled with the dirt, were added to the detergent solution and were immersed at 40°C for 2 hours, then washed in a stainless steel beaker by stirring at 100 rpm at 20°C for 10 minutes. The pieces of cloth were rinsed in running water and the reflectivity was measured after pressing with an iron. The degree of washing was calculated as follows:

Reflectivity at 460 mμ of the original cloth and dirt stained cloth before and after washing were measured (Shimadzu Seisakusho) and the degree of washing (%) was calculated.

$$\text{degree of washing}(\%) = \frac{\text{reflectivity after washing} - \text{reflectivity before washing}}{\text{reflectivity of original cloth} - \text{reflectivity before washing}} \times 100$$

Table 1 shows the average value for the 5 pieces.

The pH of the detergent solution before washing was 10.6

4) Enzyme used

(1) None (Mixture A contained mirabilite and Mixture B was balanced with water).

(2) Cellulase (origin Bacillus N-1, 2.0 units/mg of solid).

(3) Cellulase (origin Rhizopus sp., 2.1 units/mg of solid).

(4) Hemicellulase (origin Rhizopus sp., 1.8 units/mg of solid).

(5) Pectinase (origin Rhizopus sp., 1.5 units/mg of solid).

(6) Amylase (origin Rhizopus sp., 9.8 units/mg of solid).

(7) Protease (origin Rhizopus sp., 3.7 units/mg of solid).

(8) (3)/(4)/(5)/(6)/(7) = 4/1/1/1/1

5) Results

enzyme in the detergent	degree of washing (%)	
	Mixture A	Mixture B
(1) none	65	68
(2)	75	81
(3)	66	68
(4)	64	68
(5)	65	69
(6)	63	67
(7)	65	69
(8)	81	87

As shown above, the combination of cellulase produced by Rhizopus sp. and 1 or 2 or more of hemicellulase, pectinase, amylase and protease produced by Rhizopus sp. washed muddy dirt effectively.

- - - - -

Translated from Japanese by:

Quest Technology, Inc.
1603 S. Highland Avenue
Arlington Heights, IL 60005